NUCLEAR AND X-RAY TECHNIQUES

Conf-721002--1
RECEIVED BY TIC SEP 27 1972

W. S. Lyon
Analytical Chemistry Division
Oak Ridge National Laboratory*
Oak Ridge, Tennessee 37830

ABSTRACT

Nuclear and x-ray techniques provide some of the most powerful analytical methods available for the examination of environmental pollution samples. A number of the U. S. Atomic Energy Commission and National Aeronautical and Space Agency laboratories have developed capabilities in these areas to the stage where they can now accept assignments from other agencies (such as the Environmental Protection Agency) to perform specific analytical services. This paper discusses a number of these proved techniques that have been applied to environmental problems. Neutron, photon and charged particle activation analysis are examples of nuclear techniques already successfully used in pollution studies. X-ray fluorescence — induced by x-rays or charged particles — can provide elemental analysis at low cost. Electron spectroscopy for chemical analysis can provide specific chemical information about toxic elements. A few specialized techniques are also mentioned: the use of stable isotopes in environmental studies, spark source mass spectrometry for multi-element analysis,and sorption chromatography for the determination of trace organics in water. All of these methods are presently being applied and examples of data obtained from their use are given.

INTRODUCTION

An important and useful spin-off from the Atomic Energy Commission's continuing research effort has been the development of a number of nuclear and x-ray techniques applicable to the analysis of a great variety of samples. Neutron activation analysis (NAA) is probably the best known of these methods, but there are numerous others. Additionally, the requirements of the National Aeronautical and Space Agency necessitated refinements and innovations of existing technology to make possible remote analyses as well as to perform highly sophisticated examinations of returned lunar material. Recent concern about the environment has focused attention on the concentrations of many constituents in commercial products such as fuels and foods, as well as in air, water, and soil. The AEC has long been interested in environmental monitoring and a large background of information and methodology has been assembled. Thus it is not surprising to find these laboratories generating data on environmental samples. The purpose of this paper is to survey present capabilities of the national laboratories, other AEC laboratories, and NASA installations in the technologies of neutron and charged particle activation, x-ray and charged particle induced fluorescence, x-ray or particle scattering, and radioactive or non-radioactive tracers that might be used or adapted for environmental monitoring. In addition present capabilities in closely related methodologies — but not necessarily nuclear — that could be used in such monitoring are also included. Emphasis is almost exclusively on <u>present</u> techniques that are available for routine examination, but some attention is given to new techniques that may be available in the near future. We also discuss some special capabilities that make possible very unusual determinations — capabilities that can perhaps provide answers to very specific or very special questions.

In preparing this review we have contacted all the major AEC and NASA laboratories. Some of these installations expressed considerable interest in contributing material; others, either because of a present lack of capability to handle samples or some other reason (such as full committment to other programs, no interest in service work, technology not yet developed to a suitable stage for inclusion, etc.), declined to contribute. Thus this paper reflects genuine <u>in house</u> capability to perform certain determinations, and perhaps more important, genuine interest in playing an active part in the analysis of environmental samples. Obviously we could not include detailed descriptions of the facilities and experiences of every laboratory; what we have tried to

MAST

*Operated by Union Carbide Corporation for U. S. Atomic Energy Commission.

DISTRIBUTION OF THIS DOCUMENT IS UNLIM
GG

do is give the basic background information concerning the major techniques available, list some typical results obtained, and try to estimate the types and numbers of samples that could be handled — and their costs. Costs, of course, are neither easily nor firmly estimated for a general discussion such as this. The numbers given, therefore, should be viewed as preliminary and subject to firming-up when specific details are given as to types, numbers of samples and to determinations desired. Specific inquiries to specific labs should bring more specific answers.

NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis is a highly sensitive, specific, often non-destructive technique that offers the analytical chemist an opportunity to perform a number of difficult determinations in a rather straightforward manner. In its most useful form NAA requires that irradiations be made in a nuclear reactor and one ordinarily desires a high neutron flux — at least 10^{12} n-cm^{-2}-sec^{-1}. It is not a completely universally applicable technique since for a number of elements the sensitivity is rather poor, and for some there is no sensitivity at all. Neither is it a method free from errors and interferences; the experience and judgement of a trained radiochemist is required in all but the most routine of applications. In short, NAA analysis, like other analytical techniques, must be chosen discreetly, applied intelligently, and its results interpreted judiciously.

Almost all activation analyses performed today employ neutrons as the bombarding particles; probably 95 percent of all these neutron reactions involve the use of thermal neutrons. In this paper neutron will be understood to represent a thermal or 0.023 ev neutron unless otherwise stated.

When any element, E, of atomic number Z and atomic weight A is placed in a flux of neutrons, there is a finite probability that the element will capture a neutron to yield a new isotope of the same element but with a mass one unit heavier. Thus an example would be:

$$^{59}_{27}\mathrm{Co} + n \rightarrow {}^{60}_{26}\mathrm{Co} + \gamma;\ {}^{59}\mathrm{Co}(n,\gamma)^{60}\mathrm{Co} \qquad (1)$$

In Eq. (1) the notation (n,γ) indicates a neutron is absorbed and a prompt γ ray is emitted. As we shall see later nuclear reactions may be initiated by particles (p,γ) or γ rays (γ,n), and one may measure the prompt γ rays as well as γ rays from the radionuclide formed.

If the newly formed nuclide is radioactive, one may determine its presence by measurement of emitted radioactive particles or quanta. In Eq. (1) the ^{60}Co decays by beta emission followed by two quanta of energy (gamma rays):

$$^{60}_{27}\mathrm{Co} \xrightarrow[5.26y]{\beta,\gamma} {}^{60}_{28}\mathrm{Ni} \qquad (2)$$

^{60}Ni is stable so the decay chain ends; in other instances, however, several additional decay steps occur.

The production of a radioactive nuclide is given by the activation equation:

$$A = Nf\sigma\left(1 - e^{-\frac{0.693\ t}{T_{1/2}}}\right) \qquad (3)$$

where

A = disintegration rate of induced radionuclide
N = atoms of element irradiated
f = neutron or particle flux
σ = cross section of element
t = irradiation time
$T_{1/2}$ = half-life of induced radionuclide

Inspection of Eq. (3) indicates that the amount of A produced (and hence the sensitivity of any activation analysis) is a linear function of the amount of element to be determined, the flux, and the cross section. The half-life, present in the exponential term, determines the irradiation time. Obviously activities with short half-lives require only short irradiations, whereas activities of very long half-lives may be impractical for use. Neutron fluxes presently available range from 10^{11} to 10^{16} n-cm^{-2}-sec^{-1}. Cross sections of most thermal neutron capture reactions vary from 0.1 to 100 x 10^{-24} cm^2 (0.1 to 100 barns). Based on a flux of 10^{14}, irradiation time of 0.5 $T_{1/2}$ or one week, whichever is shorter, and a reasonable counting procedure, concentrations of a number of elements determinable by activation analysis are shown in Fig. 1. These values may be either raised or lowered, depending on what interferences may be present in the sample. The

important point is that the sensitivity is quite good for a number of important elements.

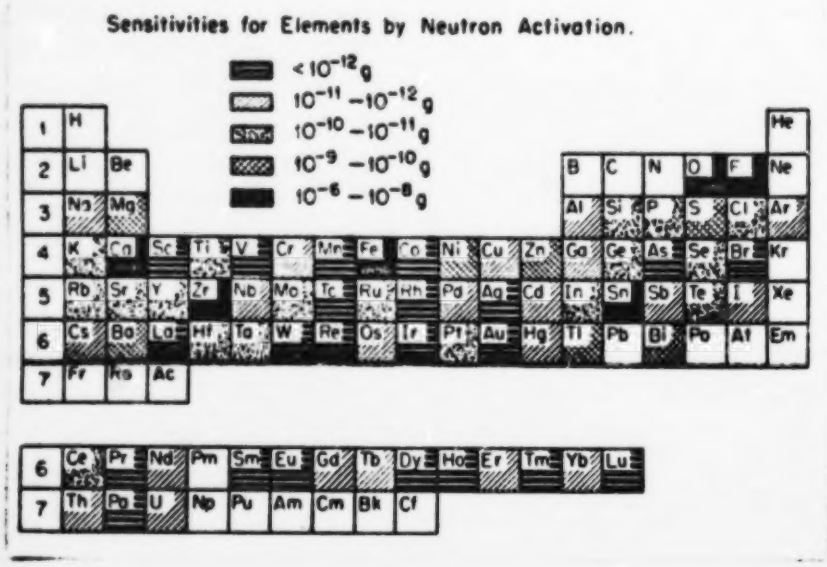

Fig. 1

Where irradiation conditions can be standardized, the neutron flux essentially constant during irradiation, and the neutron flux spectrum, the cross sections, and half-lives of the elements sought are well known, absolute activation analysis can be performed. Here one monitors only the flux (f) and calculates N from Eq. (3) by measuring A. In the past most analyses were carried out through use of a comparator technique. Here, the sample and a known standard of the element(s) to be determined are irradiated and assayed, and the amount of element in the sample found by comparison of the counting rates of standard and sample. This technique is still in great use.

After irradiation of the sample the activation analyst hopes to make his analysis with as little chemical handling as possible. Many environmental samples can be analyzed completely non-destructively, i.e. by measurement of the induced radioactivity. Unfortunately for some determinations chemical separations may be required; for example, the determination of sub-microgram quantities of Hg in coal or fly ash. The usual procedure for such samples is to irradiate sample and standard, then dissolve both, add carriers, and perform chemical separations for the desired elements. In the last step of the procedure the radioactivity of each separated and weighed precipitate is counted, and the amount of sought element calculated by comparison of sample and the standard.

High resolution Ge(Li) gamma ray spectroscopy has eliminated the need for chemistry in many activation analyses. The technique of non-destructive NAA thus consists of irradiation, measurement of the gamma ray spectra of the sample, identification and quantification of the individual gamma ray peaks, and finally calculation of the amount of element found through use of Eq. (3). The phenomena of gamma ray emission from radioactive species and its measurement by Ge(Li) gamma ray spectrometry is discussed in some detail immediately below since these subjects are of concern in almost all the nuclear and x-ray techniques that follow.

As noted in Eq. (2), when a radioactive nuclide such as ^{60}Co decays, gamma rays are often emitted. Gamma ray energies are unique for each nuclide and provide means for identification. Although one radionuclide may emit a gamma ray with an energy close to that of another, almost always there are other associated gamma rays of different energies that can be used for identification. If one knows the amount and identity of a gamma ray one has A of Eq. (3) and can thus calculate N.

When a gamma ray interacts with matter all (photoelectron production) or only part (Compton production) of its energy may be transferred. In a Ge(Li) detector such interactions can be observed with suitable electronic equipment and read out as counts per second as a function of energy. With an ideal system each gamma ray would be completely absorbed giving rise to a photoelectron that would appear as a single line in the read-out. In reality only a fraction of the gamma rays emitted by a radionuclide are absorbed, and of these only a fraction interact to produce full energy photoelectrons; the spectrum obtained is a rather level continuum of Compton electrons leading up to the photopeak, and the real life detector system has a statistical uncertainty that results in a resolution of 2–5 keV. The overall efficiency of detection is a function of size and quality of the Ge(Li) detector, and of the associated electronics. The energies of gamma rays of interest in NAA range from perhaps 0.020 MeV to 3.5 MeV. It is obvious that a large storage and analysis system is necessary to cover this range. Multi-channel analyzers for use with Ge(Li) systems have at least 1,000 channels and most users prefer

4,000. With 4,000 channels hand plotting or human interpretation of the data is impractical. Thus most users have developed computer programs or modified others' programs to analyze and interpret gamma ray spectra. These programs all depend upon a library of nuclear information (energies, half-lives, branching ratios, etc.) and require skill and intelligence in use and interpretation. Some of the basic work in developing such programs was that performed by Gunnick[1] at LLR; Heath[2] at the Idaho site has developed many programs for analysis of gamma ray spectra, not only for the AEC, but also for the NASA Lunar Receiving Laboratory. Many programs used elsewhere (e.g. that of Dyer[3] at ORNL) are based on these data.

A complete (GeLi) detector system for computerized data handling will cost from $30,000 up, and will require considerable programming and experience before it is ready for samples. Thus the available NAA facilities represent hundreds of thousands of dollars in both equipment and expertise.

NAA APPLICATION

Any laboratory with a nuclear reactor has the potential for NAA. Many, however, have only limited interest in using the technique. On the other hand, a number of laboratories have successfully applied NAA to environmental problems. Battelle Northwest Laboratories (BNWL), for example, has an extensive program in examination of soils, air, water, fish, etc. for trace element content. A highly sophisticated counting assembly employing anti-coincidence circuitry is particularly useful for very low level measurements. Typical of the work done at BNWL are the results shown in Table 1. These data were obtained by sampling the atmosphere at 3.1 Km, irradiating sample, blank, and standards, and after suitable decay period counting on the BNWL shielded multi-dimensional analyzer. These data were obtained by high-sensitivity non-destructive NAA and are part of a large study on trace element concentrations in the troposphere and lower stratosphere.[4]

Workers at Los Alamos Scientific Laboratory (LASL) have sampled a number of airborne particulates in a joint program with the U.S.A.F.[5] These aerosol samples were then analyzed by NAA, and scanning electron spectroscopy. A number of pollution sources were sampled including power plants, sawmill waste burners, smelters, gypsum plants, refineries, and urban centers. The data from these experiments provide a useful profile of trace elements in the atmosphere. For example, the trace element profiles of irradiated air-borne particulates sampled in the vicinities of two Arizona and one New Mexico copper smelters are clearly different: Re is the main radionuclide seen in the Miami, Ariz. and Hurley, N.M. samples, whereas the Douglas, Ariz. particulate shows no Re. Miami, Ariz. and Hurley, N.M. can be easily distinguished since Sm is a large component of the Hurley air particulate but is absent in Miami. This is just one example of the characterization and source-identification of air pollutants possible through the use of NAA. LASL is studying the impact of supersonic transport on the environment using similar techniques and a whole complement of analytical methodology exists there for application to pollution problems.

Oak Ridge National Laboratory has performed a number of NAA determinations for EPA. For example, Table 2 shows data obtained on coal and fly ash samples submitted by EPA. Table 3 shows a typical bunker oil analysis by NAA. Data in both tables were obtained by non-destructive NAA. Costs of these analyses are based primarily on time involved, but an average coal or ash analysis as shown probably cost $100–$300; the bunker oil somewhat less. Coal and ash are two of the worst matrices with which to work. ORNL has available fluxes up to 5×10^{15} $n\text{-}cm^{-2}\text{-}sec^{-1}$ and Ge(Li) counting systems coupled to PDP-15 analyzers for data processing. None of these three laboratories is set-up to handle thousands of routine determinations per month, but all have expressed interest in EPA work. Many of the problems involved in environmental pollution require careful evaluation and development of special activation techniques; these services are available at most of the national laboratories.

Table 1. Trace element concentrations in the atmosphere at an altitude of 3.1 kilometers, September 5, 1967[4]

Element	Exposed Filters, Micrograms/Filter	Unexposed Filters, Micrograms/Filter	Elemental Concentration, Nanograms/Standard m^3 Air
Ag	0.064 ± 0.004	0.042 ± 0.007	0.019 ± 0.008
Co	0.33 ± 0.03	0.16 ± 0.04	0.15 ± 0.05
Cr	9.2 ± 3.5	4.6 ± 3.0	4 ± 4
Fe	960 ± 80	380 ± 60	500 ± 100
Sb	0.71 ± 0.03	0.32 ± 0.04	0.34 ± 0.05
Sc	0.24 ± 0.01	0.09 ± 0.03	0.13 ± 0.03
Zn	64 ± 5	32 ± 11	28 ± 12

Table 2. Inorganic constituents in EPA samples by NAA

Element	Coal	Ash
	Per Cent	
Al	5.7	1.31
Fe	18.3	1.44
Ca	2.2	0.13
Mg	0.76	0.16
K	1.5	0.3
Na	0.23	0.032
Ti	0.26	0.068
	µg/g	
Rb	--	3.6
Ba	200	128
Mn	294	27
V	247	26
Cl	100	1,646
Br	5	26
Se	40	--
As	70	14
Sb	<7	0.7
Cd	--	--
Cs	~15	2
Co	20	12
Sc	19	3.5
La	45	8
Sm	--	--
Eu	1	0.5
Cr	100	13
Ta	<2	--
Th	25	--
U	16	1.7
W	3	3
Hg	<18	1.5
Zn	--	--
Ni	--	--

Table 3. Trace element analysis of bunker oil sample by NAA

µg/g			
Fe	11	Sc	8×10^{-4}
Mn	0.21	Cr	0.7
V	89	U	0.004
Se	0.15	Hg	0.002*
Co	0.08	Zn	1.3
		Ni	62

*Atomic absorption.

PHOTON ACTIVATION ANALYSIS

As shown in Fig. 1, there are some elements — especially in the low Z end of the periodic table — for which neutron activation has poor or no sensitivity. Many of these elements are, however, determinable by activation with photons. To produce photons an electron accelerator is required, for it is the interaction of electrons with higher Z materials (tungsten or tantalum are often used) that produce these uncharged quanta of energy. The fact that photons are uncharged makes them like neutrons — able to completely penetrate samples. Photon activation analysis (PAA) has been primarily applied to determination of trace impurities in metals, but some data have been obtained on environmental type samples. Generally speaking, PAA has never filled the need that NAA has. An excellent review on PAA was recently published[6] and numerous references to published work are given therein. Since most accelerators have been built for physics research, chemists have usually had only limited access to their use. This, coupled with the expense and

difficulty of making irradiations (construction of rabbit facilities, flux monitoring, etc.) has resulted in few routine applications. Ricci[7] at ORNL has determined experimental sensitivities for PAA at the Oak Ridge Electron Linear Accelerator (ORELA). Some of these are shown in Table 4 and indicate the excellent sensitivity for O, C, F, P, and Cd in particular. Recently (August 1972) a joint paper from the University of Maryland and the National Bureau of Standards[8] reported the use of PAA for determination of Na, Cl, Ca, Ti, Cr, Ni, Zn, As, Br, Zr, Sb, I, Ce, and Pt in air particulates.

It seems doubtful that PAA will be available for more than a few special samples — at least during the next several years. Costs should be figured on a time basis, but should run about $75 a sample.

Table 4. Sensitivities for photon-activation analysis at the ORELA[a]

Element (Target)	Product ($T_{1/2}$)	Sensitivity[b] (cpm/μg)
O(H_2O)	^{15}O(2.1m)	1,120
C	^{11}C(20.5m)	2,600
F($NaBF_3OH$)	^{18}F(110m)	5,900
Mg	^{24}Na(15.0h)	7.05
		3.37
P(red)	^{30}P(2.5m)	1,940
	^{29}Al(6.6m)	6.43
	^{28}Al(2.3m)	6.47
Ni	^{57}Ni(36.0h)	48.8
		18.8
		1.87
Cd	^{105}Cd(55.0m)	37.9
	^{111m}Cd(48.6m)	465
	^{115}Cd(53.5h)	5.37
	^{115m}In(equil.)	9.19
	^{112}Ag(3.1h)	2.74
Hg(HgS)	^{197}Hg(65h)	100
Pb(PbO)	^{204m}Pb(67m)	4.87
	^{203}Pb(52h)	127

[a] One $T_{1/2}$, max. 2h at 30 kW power.

[b] Counted on top of 3"x3" NaI(Tl).

CHARGED PARTICLE ACTIVATION ANALYSIS

Protons, deuterons, and ^3He particles from Van de Graaf machines, and charged particles (C, N, etc.) from cyclotrons have been investigated for analytical purposes. Charged particles as bombardants have several fundamental limitations: they essentially interact only at the surface of the sample, and require high energies to penetrate the coulomb barrier of the target element. ^3He activation in particular has been used for determination of low Z elements in tissue and foils, since the coulomb barrier problem here is minor. Workers at Lawrence Radiation Laboratory (LRL) at Berkeley pioneered in ^3He activation,[9] and their work has been extended and expanded by a number of workers, particularly Ricci and Hahn at ORNL. The latter have developed methods of calculating ^3He activation results and demonstrated sensitivities for many elements.[10] Some applications of this technique in the environmental and biological field include determinations of low Z elements in water, tissue, filters, but again probably not even on a semi-routine basis. Several years ago there was considerable interest in a small ^3He cyclotron to be designed specifically for analytical work. Were such a cyclotron available, we can visualize considerable use for it in environmental problems, not only for analyses, but also for production of short-lived radioisotopes of C, N, O, etc. for tracer studies. Both Philips of The Netherlands and Cyclotron Corporation of Berkeley, California have such machines available. For an excellent review of charged particle activation we recommend the article by Ricci.[11]

PROTON REACTION AND OTHER PROMPT OR SCATTERING TECHNIQUES

In the techniques mentioned heretofore, one produces a radioactive species and measures characteristic gamma-rays from its decay over a period of time after the irradiation. In proton reaction and scattering experiments the measurement is made simultaneously with the irradiation, i.e. one measures a prompt reaction product. For example, in the determination of C and N isotopic ratios in tissue ^{12}C was determined by measuring the 2.36 MeV prompt gamma from the reaction $^{12}C(p,\gamma)^{13}N$, ^{13}C by a 8.06 MeV gamma-ray from $^{13}C(p,\gamma)^{13}N$, and ^{15}N by the $^{15}N(p,\alpha\gamma)^{12}C$ reaction which gives a 4.43

MeV prompt gamma-ray.[12] Counting is done during irradiation, so one need only irradiate until sufficient data have been collected. The technique has also been applied to the determination of Li and F in salt matrices.[13]

At present the method is not available for even a semi-routine operation, but interest in it could stimulate several laboratories to provide services. Proton-reaction analysis has been suggested as one rapid method of isotopic analysis, especially for experiments employing ^{13}C (see below).

X-RAY FLUORESCENCE

When electrons are ejected from inner orbitals of an atom their replacement results in the emission of x-rays. K x-rays are produced by filling the innermost or K orbital, L x-rays from the L orbital, etc. The energies of K or L x-rays are characteristic of the element; thus measurement of these x-rays can be a unique identification of an element.

Electrons can be removed from an atom by a number of means — charged particles and electrons, as we shall see later, have recently been used. But the most commonly used method employs x-rays from an x-ray tube, hence the name x-ray fluorescence analysis (XRF). X-rays can also be produced by a radioisotope source (^{241}Am, ^{109}Cd, etc.) or by beta-particle induced bremstrallung. Radioisotope x-ray spectrometry was the subject of a 1966 review,[14] while a general review of the whole subject was published in 1970.[15]

In its simplest form an x-ray fluorescence analysis system might consist of an x-ray tube (or radioisotope source), some type of collimator to sharpen up the x-rays, the sample upon which the x-rays fall, and a detector and electronics to measure and record the fluorescent x-rays that are produced. The Ge(Li) detector that is used in gamma-ray spectrometry is also used here, except its size can be much smaller since we are dealing with low energy (<80 keV) x-rays rather than gamma rays. The Ge(Li) detector can be manufactured with resolutions approaching 1 keV, and for very low-energy x-rays Si detectors have been used. Again one follows the detector with a multi-channel analyzer and read-out.

X-ray fluorescence analysis becomes less practical as the Z of the desired element decreases. Below $\sim Z = 19$ the method becomes subject to difficulties that make it advisable to look to other techniques. One reason for this is, of course, the dropoff of x-ray energy with Z; at lower x-ray energies the absorption of these x-rays by the matrix becomes larger and one reaches the point where losses are quite appreciable. A more fundamental limitation is the fluorescence yield.

When (say) an L electron falls into a K level vacancy (created by removal of the K electron) the energy difference between the K- and L- binding energies may be emitted as a characteristic x-ray, or may be used in an internal photoelectric process that results in emission of an additional electron from the L, or M, etc. shell; the whole process may result in many x-ray and electron emissions (Auger electrons). The fluorescence yield (ω_f) is the fraction of vacancies that are filled by x-ray emissions and increases with Z from about $Z = 15$ $\omega_f = 0.05$ to $Z = 70$, $\omega_f = 0.9$. There is also fluorescence yield for L x-ray emission. Another complicating factor is the competition between photoelectric and Compton interaction as scattered radiation interacts with the sample and surroundings. This results in a background continuum with peaks in the x-ray spectrum. Present and immediate future technology aims at computer resolution and calculation of such x-ray peaks much in the manner previously described for gamma-ray resolution.

X-ray fluorescence is rapid, inexpensive, quite sensitive for middle Z elements, and highly reliable. It has already been applied for elemental determinations in a number of environmental samples. Goulding,[16] for example, has shown its applicability to determinations in food, vegetation, fish and other aquatic organisms, and air filters. Figure 2, taken from Goulding, shows an x-ray spectrum obtained from an air filter. Most of the major AEC laboratories have XRF capability, but none is at present engaged in running large numbers of service analyses. Interest has been expressed by several in setting up a facility for such work if a demand exists. Costs should be <$10 per sample; this would include measurement of perhaps 8 or 10 elements. Six-ten samples per hour per instrument seems a reasonable sample load estimate.

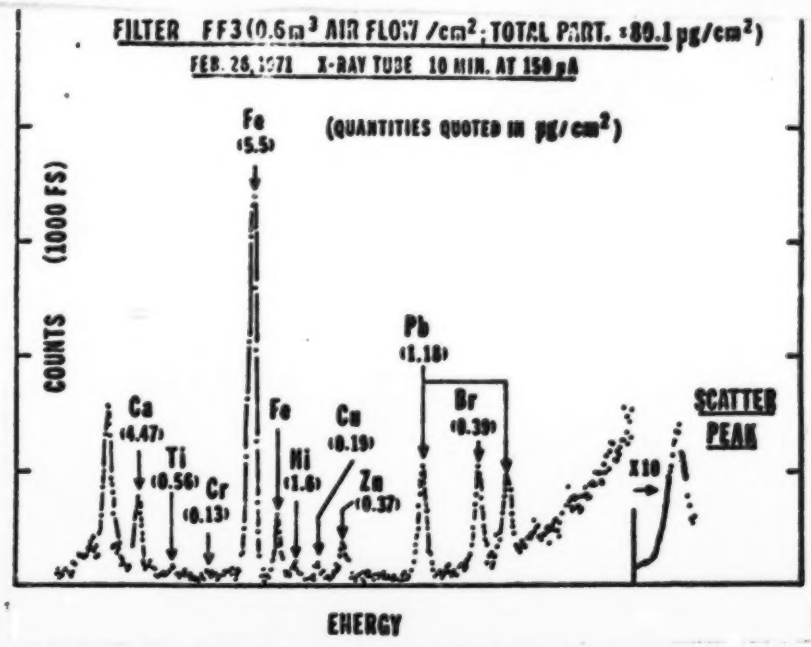

Fig. 2. Trace elements in an air filter determined by XRF

The ultimate limit of detectability in XRF depends upon the magnitude of the x-ray peak relative to background; this latter is directly related to scattering and the magnitude of unwanted "white x-rays" from the x-ray source, and secondary x-rays from interaction of the fluorescent x-rays with surroundings. Sparks,[17] at ORNL has under development at the present time a double monochromator system: a compression annealed pyrolytic graphite monochromator to reduce "white" radiation from the target, and a second doubly curved monochromator placed between sample and detector to reduce scattered radiation. Preliminary data indicate this combination can drastically reduce the background; Fig. 3 shows data obtained for Hg with an x-ray tube with one and both monochromators in place. Note that L x-rays are being measured here. The Si(Li) detector has better resolution than Ge(Li) but much poorer efficiency as a function of energy. Thus one chooses to measure the 10 keV L x-ray rather than the 70 keV K x-ray. The present detectable limit for Hg appears to be 0.2 µg/g. This equipment is still in the development stage, but the ultimate goal is a completely automated XRF system with automatic sample changer, double monochromator, and computer operated and corrected data processing system. Present estimate is 18 months to completion. Costs should be less than those estimated previously.

Radioisotope x-ray sources have several characteristics that make them highly desirable for specific applications. First and most obvious is their simplicity relative to an x-ray tube: no power requirement and no large amount of shielding. A single x-ray energy is available without the use of a monochromator when one uses an x-ray emitting nuclide such as ^{241}Am or ^{109}Cd. One can also make an x-ray source of a particular energy by a secondary technique: let beta radiation fall on an element whose characteristic K x-ray energy is desired. One immediately obvious limitation of this latter method is the very low efficiency of the process. Rather simple x-ray fluorescence units have been designed from radioisotope sources for field use and where only modest sensitivity is required these units are quite satisfactory. In general, however, they cannot compete with a good tube system.

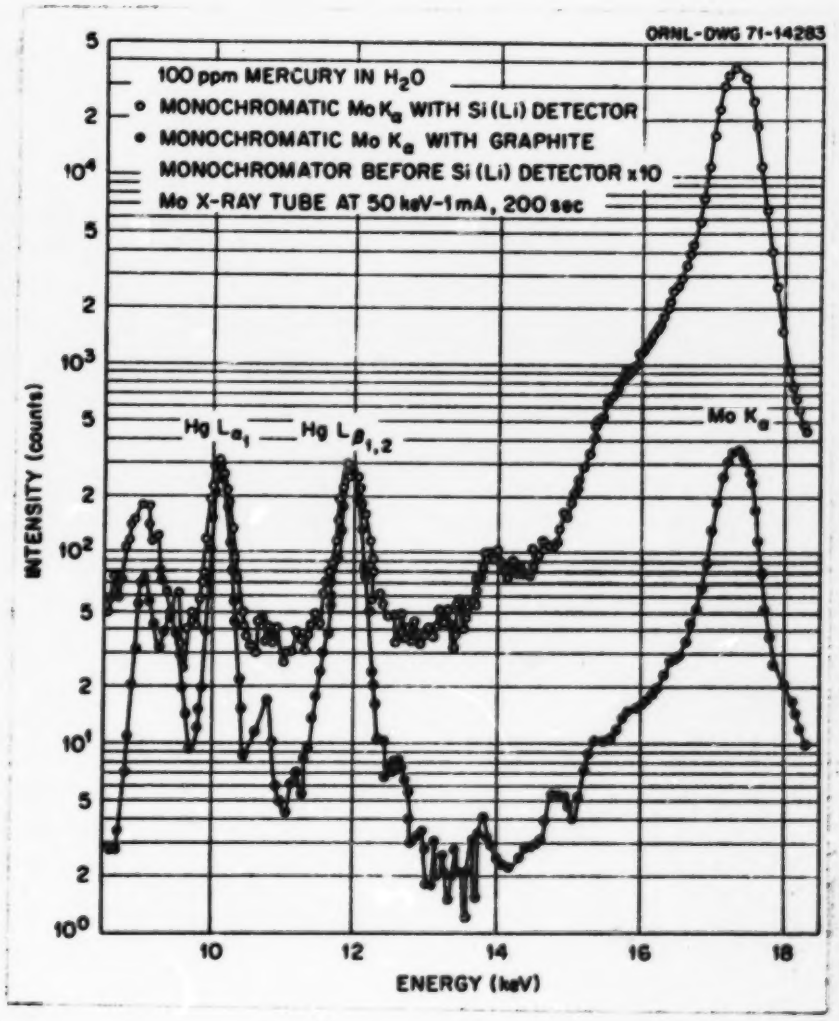
ORNL-DWG 71-14283
100 ppm MERCURY IN H2O
• MONOCHROMATIC Mo Kα WITH Si(Li) DETECTOR
• MONOCHROMATIC Mo Kα WITH GRAPHITE MONOCHROMATOR BEFORE Si(Li) DETECTOR x10
Mo X-RAY TUBE AT 50 keV-1 mA, 200 sec
INTENSITY (counts)
Hg Lα1
Hg Lβ1,2
Mo Kα
ENERGY (keV)

Fig. 3. Determination of Hg in H_2O by XRF and a monochromator system[17]

CHARGED PARTICLE INDUCED X-RAY FLUORESCENCE

Not only x-rays induce x-ray fluorescence; electrons and charged particles such as photons and alpha particles can also be used. The maximum cross section for a given target element is directly proportional to the square of the charge of the projectile and occurs at projectile energies that are directly proportional to the projectile mass. Electron induced x-ray excitation

results in a large bremsstrahlung background. Charged particle x-ray excitation (CPXE) produces significantly less background; for example the rate for 50 MeV protons is about 10^6 times less than that for 20 kw electrons. As discussed in the section concerned with charged particle activation analysis, these techniques require the use of large machines — cyclotrons or Van de Graafs. Thus, until recent changes in emphasis on directions of research, little time or interest was forthcoming from physicists or their machines. This has now changed; this spring physicists[18] at ORNL used oxygen ions to study La adsorbed on rock salt by CPXE. The results from this investigation are of interest in predicting behavior of fission products stored in salt mines.

A considerable research and development effort on CPXE at Brookhaven National Laboratory (BNL) is expected to culminate in a routine automated analysis system by 1974. Beam lines will be set up at the RARAF (Medical Accelerator) specifically for this purpose. Gordon and co-workers at BNL have published a number of informative papers[19,20] on CPXE describing experiments using a number of accelerators and projectiles. They have obtained data using cancerous tissue, soil, air filters, and biological material as targets. Figure 4 shows data obtained using NBS orchard leaves as the target. An 8-minute irradiation at 17.5 nanoamps with 3.5 MeV protons was made with the orchard leaves backed by 3.5 mg/cm^2 millipore filter. The identifying element symbol and x-ray line are shown along the abcissa. The numbers at the end represent the deviation in ev between the observed and true x-ray energies.

CPXE seems to be one of the most promising of the new nuclear techniques. The projected BNL CPXE laboratory should be able to handle 50 samples per 8-hour day at a cost of ~$10/sample. Perhaps 9 elements could be reported in each sample. Thus a low cost of $1/element seems possible.

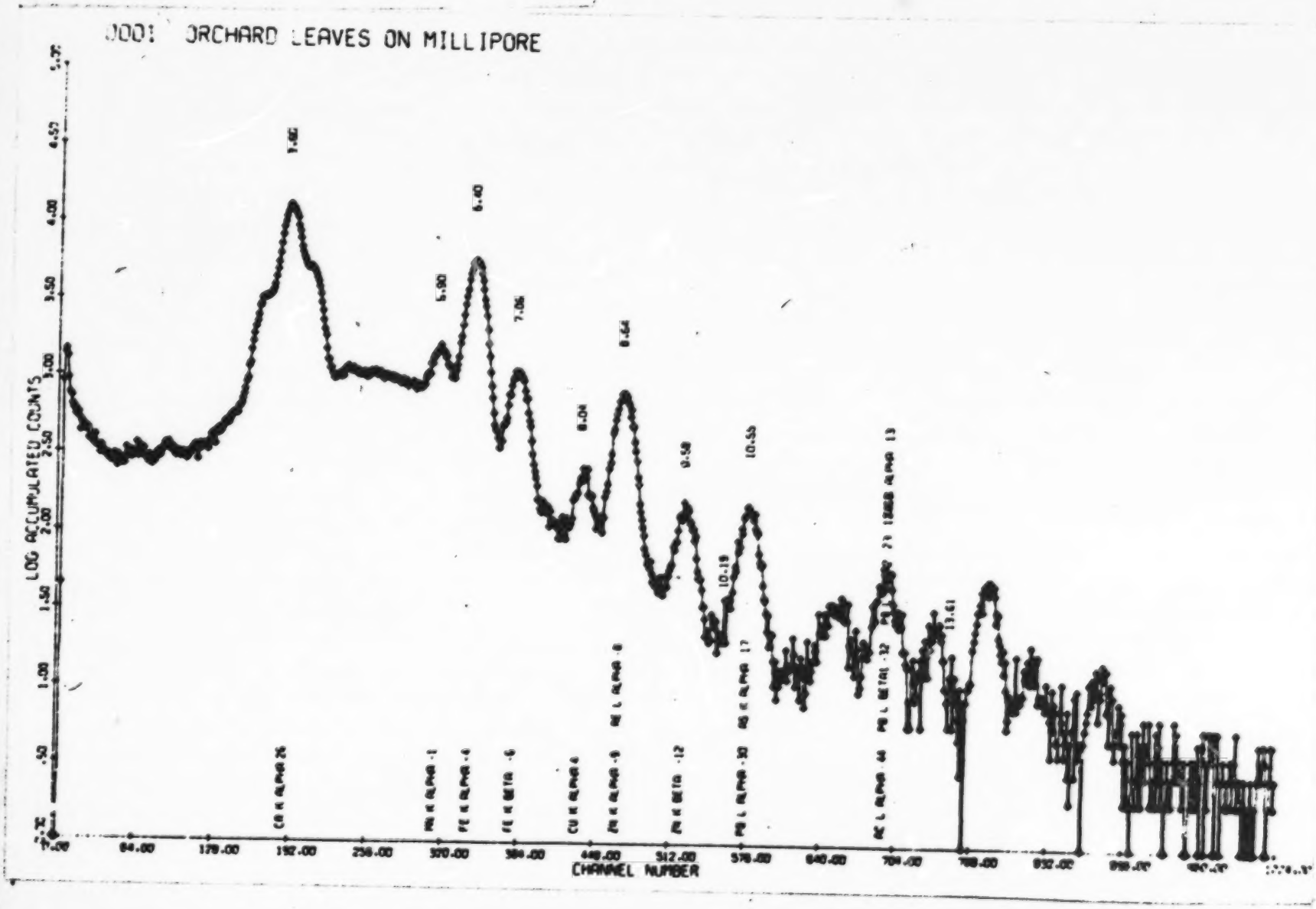

Fig. 4. X-ray spectra obtained by CPXE of NBS orchard leaves [20]

Certain problems appear universal in all these x-ray fluorescence techniques, however, and although they are somewhat akin to similar problems in activation analysis, they are not identical. The main difficulty is the interpretation and elucidation of the x-ray spectrum — particularly the identification of small peaks from minor constituents. This ability has not yet been really satisfactorily demonstrated. In NAA two ways exist to by-pass or at least ameliorate this problem: use of several gamma-ray peaks from the same radionuclide and/or allowing some components to decay out before measuring others. As demonstrated in Fig. 4 the components identified are major ones. The technique must be tested for smaller components; for example, Hg is known to be present in this sample at ∿0.15 μg/g. A slight indication of a peak in Fig. 4 to the left and below the 10.19 keV peak may be Hg. This problem is under continuing study at BNL.

Cooper[21] of BNWL has just completed an experimental study of sensitivities of particle and photon excitation methods of x-ray fluorescence for analysis of trace elements in environmental samples. His conclusions: results indicate that low energy proton excitation techniques do not exhibit analysis capabilities significantly different from those of photon excitation methods while high energy alpha excitation is not competitive. These results are so recent (Aug. 31, 1972) that other workers have not had time to study them carefully or to attempt confirmation.

ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS

A weakness of most nuclear and x-ray techniques is that they are unable to present any information concerning the chemical state of the element in question. A method that does provide such chemical information by an x-ray technique is electron spectroscopy for chemical analysis (ESCA). ESCA is a technique whereby one deduces binding energies of inner core electrons of an atom — which are sensitive to the chemical environment — from high resolution measurements of spectra of photoelectrons produced by x-rays. The use of ESCA has been extended to organic chemistry also, with the observation that it is possible to differentiate spectra from the carboxyl carbon atom and the benzene carbon. Similar observations have been made for compounds containing nitrogen, oxygen, and sulfur.

Because of the complexity of the equipment (a double focusing iron-free magnetic electron spectrometer is required) and sophistication of the method, ESCA is presently only being applied to a limited extent for special problems. It does offer the ability to elicit otherwise unobtainable chemical bonding information by physical means. For example, at ORNL Hulett[22] has investigated the chemical form of sulfur in smoke particles using ESCA. In Fig.5 we see the photoelectron spectra of sulfur on smoke particles, fly ash, and (at top) reference sulfate. The sulfur in both smoke and fly ash exhibits a shift. The coal smoke particles exhibit a peak at ∿165 ev that is probably sulfide or a mercaptan; the doublet at ∿170 ev is indicative of two higher oxidation species — sulfite and sulfate. The flyash spectrum shows two peaks probably sulfate and adsorbed SO_3. The possibilities latent in this technique are quite apparent and effort continues to develop it.

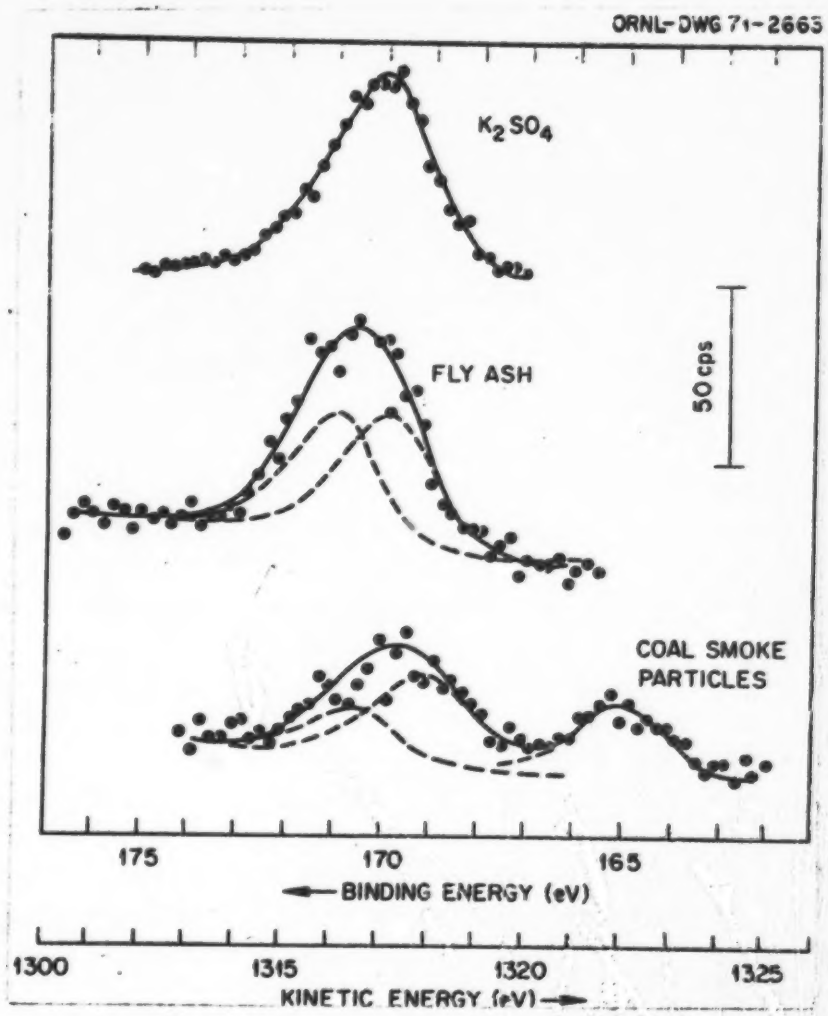

Fig. 5. Photoelectron spectra of sulfur on various substrates.[22]

STABLE AND RADIOACTIVE TRACERS

The contributions of radioactive tracer techniques to a better understanding of industrial, chemical, biological, and physical processes fill a number of books and reviews. Strangely, however, few tracer techniques have been successfully adapted as analytical techniques. Thickness gauges appear to be the outstanding analytical radioisotope application. Of course ^{14}C, ^{32}P, ^{35}S and other radionuclides have provided basic understanding or aided in testing many analytical methods. A general overview of the subject is available in an IAEA Conference Proceedings volume.[23]

Stable isotopes have been used in conjunction with NAA or some other analytical technique for a number of investigations. Los Alamos Scientific Laboratory is now producing 5 Kg/year of ^{13}C and will soon raise this to 40-50 Kg/year. Their ICONS program will make ^{13}C, ^{15}N, ^{17}O, ^{18}O available for ecological investigations. Nitrogen depleted in ^{15}N is now available in large quantities for field studies such as fertilizer run off. Triply labelled CO_2 (^{13}C and ^{18}O) with its mass of 49 can be used for atmospheric tracing. These tracers can be used only if sensitive, accurate analytical techniques are available. Charged particle and neutron activation can provide such service; spark source mass spectrometry (see below) can also perform these determinations. Present cost of ^{13}C is \$60/g; ^{18}O, \$100/g.

SPECIALIZED NON-NUCLEAR TECHNIQUES

The facilities of AEC and NASA laboratories are obviously not limited to the nuclear and x-ray techniques discussed above. Analytical chemistry has been an important adjunct in the development of nuclear power, and virtually every modern analytical instrument and technique is available and in use at these facilities. It is beyond the purpose of this paper to discuss the conventional techniques, but two examples of highly sophisticated non-nuclear analytical techniques will be briefly mentioned since both have been used to analyze environmental pollution type samples and both are available to outside customers for additional services. These two techniques are 1) spark source mass spectrometry (SSMS) for elemental identification, and 2) sorption, gas chromatography, and mass spectrometry for identification of organic impurities in water.

SPARK SOURCE MASS SPECTROMETRY

Mass spectrometry is one of the most sensitive and comprehensive techniques of trace analysis in inorganic systems. A mass spectrometer separates gaseous ions according to their mass-to-charge ratios (m/e) by the action of electric and/or magnetic fields and records these ratios and their relative intensities. A mass spectrometer consists of four essential aspects: 1) the source, which produces a beam of ions representative of the sample, 2) the analyzer, in which the separation is effected either in space or in time, 3) the detector, where the resolved ions are detected and their number is counted, and 4) the vacuum system, which provides the environment for all these processes.

The most useful mass spectrometric method for general analysis employs the vacuum spark source. In this source a high-voltage radio-frequency discharge (50-150 kV) is produced between two closely spaced electrodes of the material to be analyzed. In the source region the two electrodes are sparked resulting in vaporization and ionization of the sample constituents. After acceleration of the ions into the slit system, the electrostatic analyzer selects for transmission ions of a certain energy range, with no mass separation. The magnetic field separates the ion beam according to mass-to-charge ratio, providing mass analysis at the same time. The ions may be recorded either electrically or photographically. Spark source mass spectrometry is a multielement technique, capable of detecting trace elements at the parts per billion level, with applicability to the entire periodic table.

Detection limits for most elements are 0.5×10^{-9} grams or lower. The data as recorded by SSMS are generally good to $\pm$50%; to obtain a quantitative value one must use an isotope dilution technique. Here a known amount of an enriched stable isotope of the element(s) in question is added as an internal standard. Usually only 3 or 4 "isotope spikes" can be added in any one determination. For many samples, however, elements can be referenced to one constituent which is quantitatively known, e.g. to Fe in coal

ash samples. The SSMS is an expensive piece of equipment but most national laboratories have several available.

Oak Ridge has performed a number of special analyses for EPA as well as provided them with consultation in setting up new SSMS laboratories. Lead in gasoline has been determined quantitatively by synthesizing an organic standard solution containing a known amount of ^{204}Pb. Values of Pb ranging from 0.07 to 3 grams per gallon of gasoline have been determined. Isotope dilution has also been used to determine Hg and Cd in various matrices including vegetation, soil, gas, oil, coal, and ash. Values as low as 0.01 µg/ml are easily seen.

Bunker heating oil is a heavy viscous liquid (essentially a solid at room temperature) and a most difficult matrice to work with. Table 5 lists typical results from a SSMS analysis of such a sample.

Table 5. Weight ppm trace metals in bunker oil sample by SSMS

Ag	0.1	Mg	2
Al	20	Mn	1
As	0.7	Mo	0.2
B	0.05	Na	1
Be	<0.01	Ni	70
Bi	<0.1	P	2
Hg	0.005*	Pb	3
Cd	0.83*	Si	30
Co	1	Ti	0.3
Cr	1	V	100
Cu	0.3	Zn	2
Fe	20	Zr	0.2
K	1	Se	0.02
Li	0.03	S	>100

*Isotope dilution.

Costs for SSMS will run about $150 for a series of quantitative determinations of up to 50 elements in one sample. For isotope dilution analysis the cost will be ∿$100; at ORNL isotope dilution can be run for U, Hg, Cd, Pb, Zn, and Fe.

One important service a SSMS laboratory can perform is that of reference analysis. The SSMS lab might periodically check samples that have been analyzed by other laboratories and other techniques. The referee lab concept seems highly desirable for Cd and Hg analysis in particular.

There are, of course, a number of other spectrometric analytical techniques available for single and multi-element analysis; to discuss all of these is beyond the scope of this paper. Atomic absorption is a widely used single element technique, emission spectroscopy a multi-element one. Recent innovations in the latter technique such as induction coupled plasma excitation have greatly extended its range and capability. Iowa State,[24] for example, has under development a highly sophisticated system for multi-element analysis. Costs for analysis using this technique should be quite reasonable.

ORGANIC IMPURITIES IN WATER

A general lack of information exists about the organic content of water primarily because there is no generally applicable method for concentrating, separating, and identifying soluble organic compounds which may be present at concentrations less than one milligram per liter. A group at the Institute for Atomic Research, Iowa State University, Ames, Iowa has recently developed and demonstrated a system that can solve this problem. Simply stated their method involves quantitative sorption of trace organic compounds on a macroreticular resin bed followed by selective desorption using appropriate eluents. Identifications of the compounds present are made with a gas chromatograph-mass spectrometer combination. In addition identification can be confirmed by comparing gas chromatographic retention times and ultraviolet, infrared, proton magnetic resonance, and mass spectra with known samples. In one experiment water from a series of wells in Ames was analyzed and a number of impurities definitely established.[25] Table 6 gives results from one such well. Concentrations of some of the constituents not determined at the time of analysis could have been obtained with additional effort. This system is still under development but is available for service work part time. Charges will be made on a man-hour basis. For determinations of levels of neutral organic constituents cost would be ∿$50; to identify compounds requested by sender (i.e. DDT) ∿$80 or $40 per compound plus $50 basic charge for the chromatogram. A complete analysis of an unknown might run from several hundred dollars to several thousand. In all cases users should first contact

Ames personnel[26] for advice concerning sampling precautions. The technique would seem to fill an important need in environmental analysis.

Table 6. Neutral compounds in a contaminated Ames, Iowa well

Name of component	Concentration, ppb	Std dev
Acenaphthylene	19.3	1.4
1-Methylnaphthalene	11.0	0.6
Methylindenes (two isomers)	18.8	0.8
Indene	18.0	1.5
Acenaphthene	1.7	0.2
2-2-Benzothiophene	0.37	0.11
Isopropylbenzene)		
Ethyl benzene)		
Naphthalene)		
2,3-Dihydroindene)	15	
Alkyl-2,3-dihydroindene)		
Alkyl benzenes)		
Alkyl benzothiophenes)		
Alkyl naphthalenes)		

SUMMARY

A number of x-ray and nuclear techniques are available at AEC and NASA laboratories for determination of inorganic constituents in environmental samples and for organic constituents in water. We have indicated typical results obtained by use of these techniques with variety of matrices; additional information may be found in referenced material.

ACKNOWLEDGEMENTS

The author would like to express his appreciation to each of the scientists who supplied him with data and information concerning his own special technique. Space limitations prevent individual listings just as it has prevented an exhaustive discussion of each method. Without this assistance the task of writing this paper would have been most onerous indeed.

REFERENCES

1. R. Gunnick et al, "Identification and Determination of Gamma Emitters by Computer Analysis of Ge(Li) Spectra," LRL UCID 15140 (May 16, 1967).

2. R. L. Heath, in Modern Trends in Activation Analysis, ed. by J. R. de Voe, NBS Spec. Publ. 312, Washington, D. C., 1969, Vol. II, p. 959.

3. A. Houtzeel, F. F. Dyer, "A Study of Fission Products in the Molten-Salt Reactor Experiment by Gamma Spectrometry," ORNL-TM-3151 (Aug. 1972).

4. L. A. Ranticelli, R. W. Perkins, J. Geophys. Res. 75, 3055 (1970).

5. W. A. Sedlacek, P. R. Guthals, H. L. Smith, "Identification of Aerosols in the Southwestern United States Using Activation Analysis and Scanning Electron Microscopy," LA-DC 13316 (1971).

6. G. J. Lutz, Anal. Chem. 43, 93 (1971).

7. E. Ricci, in Analytical Chemistry Division Annual Progress Report for Period Ending September 30, 1971, ed. by W. S. Lyon, ORNL-4749, p. 36 (1972).

8. N. K. Aras, W. H. Zoller, and G. E. Gordon, Abstracts of Papers, 164th National Meeting American Chemical Society, New York City, August 27-Sept. 1, 1972 (ACS, Washington, D. C.), NUCL 27.

9. S. S. Markowitz, J. D. Mahoney, Anal. Chem. 34, 329 (1962).

10. E. Ricci, R. L. Hahn, Anal. Chem. 40, 54 (1968).

11. E. Ricci, in Advances in Activation Analysis, ed. by J.M.A. Lenihan, S. J. Thompson, V. P. Guinn, Academic Press, London, 1972, Vol. 2, p. 221.

REFERENCES (Continued)

12. E. Ricci, Anal. Chem. 43, 1266 (1971).

13. R. L. Macklin et al, Nucl. Appl. 5, 269 (1968).

14. J. R. Rhodes, Analyst 91, 683 (1966).

15. K. G. Carr-Brion, K. W. Payne, Analyst 95, 977 (1970).

16. F. S. Goulding, J. M. Jaklevic, "Trace Element Analysis by X-Ray Fluorescence," UCRL-20625 (1971).

17. R. W. Gould, S. R. Bates, C. J. Sparks, Appl. Spect. 22, 549 (1968).

18. M. I. Saltmarsh, A. Van der Woude, C. A. Ludemann, Appl. Phys. Lett. 21, 64 (1972).

19. B. M. Gordon, H. W. Kraner, in Trace Substances in Environmental Health — V, ed. by D. D. Hemphill, Univ. of Missouri, Columbia, Mo., 1971, p. 419.

20. B. M. Gordon, H. W. Kraner, J. Radioanal. Chem. (in press).

21. J. A. Cooper, "Comparison of Particle and Photon Excited X-ray Fluorescence Applied to Trace Element Measurements of Environmental Samples," BNWL SA 4304 (Aug. 31, 1972).

22. L. D. Hulett, T. H. Carlson, B. R. Fish, J. A. Durham, in Determination of Air Quality, ed. by G. Mamantov, W. D. Shults (Plenum Press, N. Y. 1972), p. 179.

23. I.A.E.A., Nuclear Techniques in Environmental Pollution. Proceedings of a Conference, Salzburg, Austria, 26-30 October 1970, IAEA, Vienna (1971)

24 G. W. Dickinson, V. A. Fassel, Anal. Chem. 41, 1021 (1969).

25. A. K. Burnham et al, Anal. Chem. 44, 139 (1972).

26. G. V. Calder, Ames Laboratory, USAEC, Ames, Iowa (private communication, Sept. 1972).

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.